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(1 soft copy to Dr. Ullal; 1 hard copy to Ms. C. Lopez)

Re: Ninth Monthly Report on Pulsed Light Annealing #NDJ-2-30630-11 Mod 6

Dear Harin,

This letter comprises the ninth monthly technical status report for "CIGS Film Fabrication by Pulsed Light Annealing of Precursor Films", which is a task added as Mod 6 to ITN's subcontract #NDJ-2-30630-11, "Plasma-Assisted Coevaporation of S and Se for Wide Band Gap Chalcopyrite Photovoltaics", under the Thin Film Partnership Program. This letter describes work performed during the reporting period of May 15, 2003 through June 14, 2004.

Goals and Approach

The primary objective of this research effort is to demonstrate the production of high-efficiency thin-film CIGS solar cells on polyimide substrates by using high-rate heating from a super-intense pulsed light source. The heating rates to be investigated (millisecond time-scale) are at least two orders of magnitude higher than those reported in previous efforts that use Rapid Thermal Processing (RTP) to convert precursor materials to CIGS films for photovoltaics. Higher heating rates may be advantageous in that (1) thermal degradation of the substrate may be avoided with fast annealing and, (2) diffusion of gallium to the back of the film, which is a major limitation encountered in other CIGS RTP work, may be dramatically reduced. Goals of the present investigation are to determine the viability and challenges of using short (<50 ms) pulses from a super intense light source to:

- Convert sputter-deposited precursor films to chalcopyrite-phase CIGS.
- Improve co-evaporated CIGS electrical properties and thereby allow the use of lower deposition temperatures while retaining device performance.
- Develop a method for CIGS film production that is well suited for production scale-up and capable of producing efficiencies that match those achieved using high-temperature co-evaporation.

An additional goal will be to determine whether high-rate heating can effectively eliminate thru-film and lateral diffusion of elements during conversion of precursor structures to produce CIGS films with high front-side gallium content.

Activities

During the current reporting period, the second round of pulsed light annealing experiments was completed. This round of experiments included precursor films of three structures (which we refer to as type C, D, and E) on two types of substrates (molybdenum-coated polyimide and molybdenum-coated stainless steel). Pulsed-light annealing converted some of the precursors films to single-phase or nearly single-phase CIGS. Evaporated CIGS films on polyimide and stainless steel substrates were also subjected to pulsed-light annealing and then finished into devices. A significant result was that CIGS films on polyimide were heated to temperatures as high as 560 °C without embrittlement or significant deformation of the substrate. The performance of devices made from the evaporated CIGS subjected to pulsed-light annealing was generally worse than devices made from control films that did not received pulsed-light annealing. These results are presented in more detail below.

Precursor film Conversion

Samples for precursor conversion in the second round of pulsed-light annealing experiments consisted of precursor films of three structures (referred to here as types C, D, and E) on molybdenum-coated stainless steel (SS) substrates and molybdenum-coated polyimide substrates (PI). Spectral reflectance measurements for use in thermal modeling were performed on each type of sample in the as-deposited state. Each sample was then treated with a single pulse of light with an approximate duration of 20 ms. Two or three fluence levels (i.e. J/cm^2) were tried for each combination of film type and substrate type. Fluence levels were selected based on thermal modeling for prediction of the film temperature during pulsed-light annealing. For samples on PI substrates, fluence values were used that were predicted to result in a maximum film temperature of approximately 520, 560, or 615 °C. For samples on SS substrates, fluence values were used that gave a predicted maximum film temperature of 560, 650, 700, or 800 °C.

Figure 1 shows the precursor CIGS samples in plastic boxes after pulsed-light annealing. All films heated to temperatures above 520 °C exhibited a notable change in color and appearance with pulsed-light annealing. For most samples, at least part of the film lifted from the substrate to form “blisters” or delaminated regions either during pulsed-light treatment or during the return shipment from the laboratory where the pulsed-light annealing was conducted. For the samples on stainless steel substrates, only the highest temperature (800 °C) treatment resulted in deformation of the substrate. The appearance of this film was also the most striking as it exhibited speckles of multiple colors. An important result is that none of the polyimide substrates became brittle or significantly deformed as a result of the pulsed-light annealing, even in the cases for which the modeling predicted that the film temperature exceeded 600 °C. From previous work we know that heating polyimide foil to temperatures in excess of 500 °C for a period of 10 minutes causes severe embrittlement of the polyimide. This fact limits the substrate temperature that can be used and the efficiencies that can be achieved when depositing CIGS on polyimide in a conventional evaporation process. If our temperature modeling predictions are correct, then we have demonstrated that pulsed-light annealing allows heating of a CIGS film on polyimide to higher temperatures than would normally be possible without substrate degradation.

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Figure 1: Photograph of CIGS precursor films following pulsed-light annealing. The labels indicate the film type (C, D, or E), substrate type (SS for stainless steel and PI for polyimide), and the maximum temperature that the precursor film reached during annealing as predicted by modeling.

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X-ray diffraction (XRD) analysis showed that none of the type C precursor films were successful converted into CIGS without the presence of significant concentrations of copper selenide and other phases. Figure 2 shows XRD spectra for as-deposited and pulsed-light annealed type C precursor films on stainless steel substrates. Emergence of the CIGS 112, 220, and 312 peaks in the spectra for the film heated to 563 °C indicates that CIGS formation occurred during treatment, but peaks corresponding to Cu_3Se_2 and elemental Se indicate the presence of these other phases as well. For the film heated to 646 °C, the Cu_3Se_2 101 peak intensity was even higher than that of the CIGS 112 peak. Cu_3Se_2 peaks also dominated the XRD spectra of type C films on polyimide substrates (not shown).

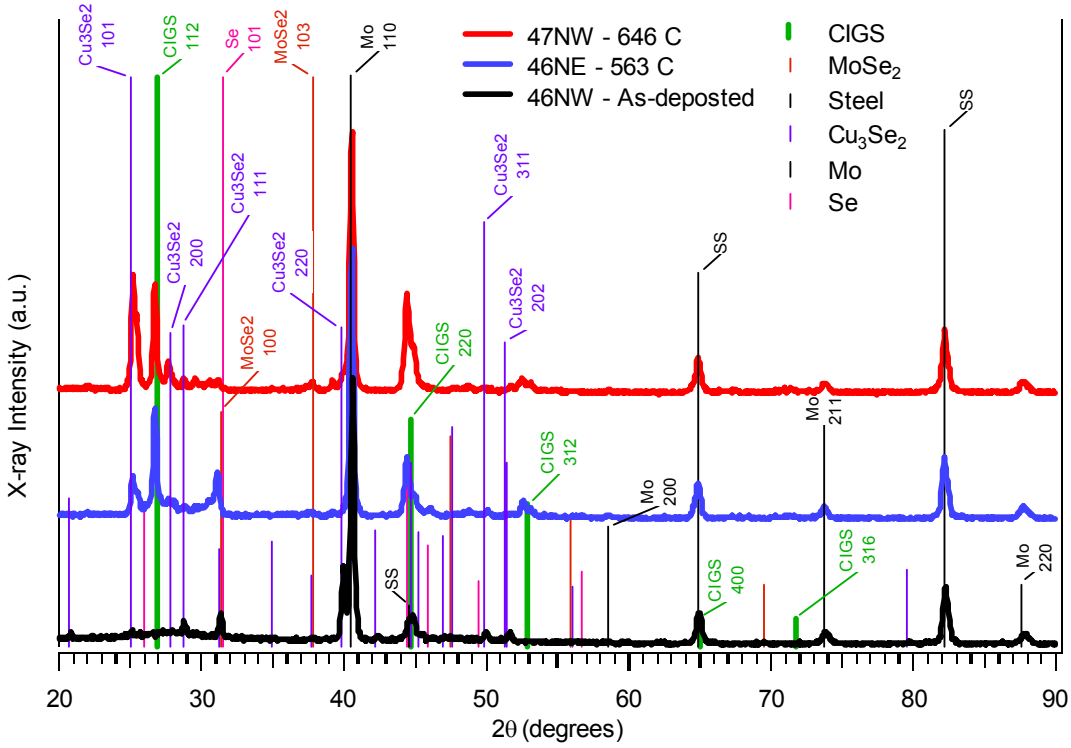

Figure 2: XRD spectra of type C precursor films on stainless steel substrates in the as-deposited state, after pulsed-light annealing to a temperature of 563 °C, and after pulsed light annealing to a temperature of 646 °C. Vertical lines show the peak positions and relative intensities for various phases from JCPDS powder diffraction standards.

Pulsed-light annealing of type D precursor films on SS substrates resulted in nearly complete conversion of the films to single-phase CIGS. Figure 3 shows the XRD spectra for the type D films on stainless steel substrates. Peaks corresponding to CIGS, molybdenum, and stainless steel dominate the spectra. Very small peaks corresponding to Cu_3Se_2 are also present, although at the higher treatment temperature these peaks are nearly unobservable. Strikingly different XRD spectra (Figure 4) were found for type D films on polyimide substrates. The type D films on PI substrates were found to contain significant quantities of elemental Se and Cu_3Se_2. For the highest treatment temperature, In_2Se_3 was also observed. The difference between the SS and PI substrate results is likely to be due to the significantly shorter time that temperature of the films on polyimide stays near its maximum value as shown by the modeling results reported in previous months.

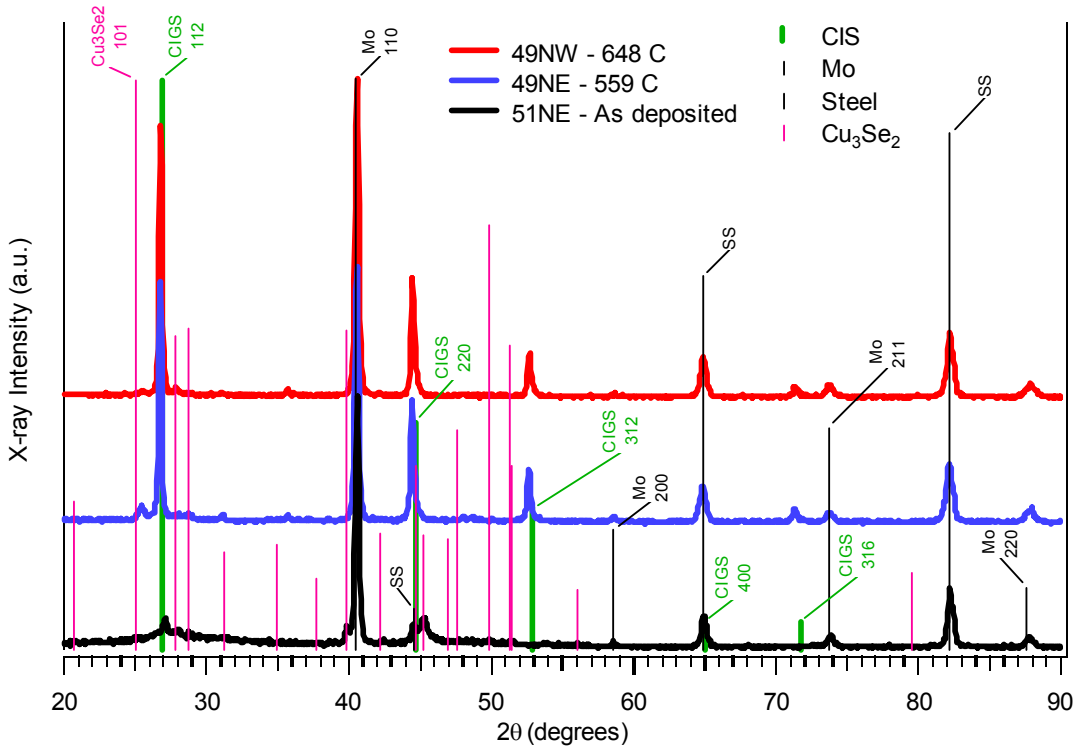

Figure 3: XRD spectra of type D precursor films on stainless steel substrates in the as-deposited state and after pulsed-light annealing.

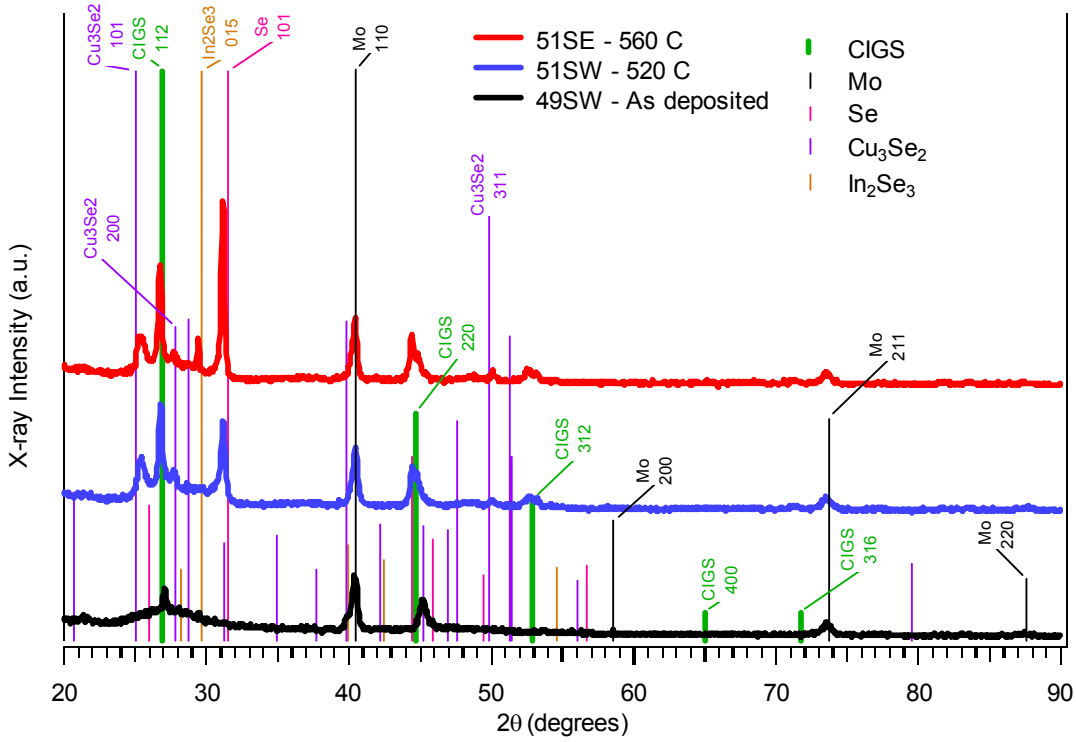

Figure 4: XRD spectra of type D precursor films on polyimide substrates in the as-deposited state and after pulsed-light annealing.

From the point of view of obtaining single-phase CIGS, the best results were obtained with type E films. Figure 5 and Figure 6 show the XRD spectra of type E films on SS and PI substrates, respectively. The as-deposited type E films show small diffraction peaks corresponding to the CIGS 112 and 312 planes suggesting that some CIGS formation took place during film deposition. With pulsed-light annealing, these peaks grow significantly and the CIGS 220 and 316 peaks also emerge. Small bumps at $2\theta = 25.5°$ in the spectra for the as-deposited films suggest the presence of a small amount of Cu_3Se_2. While this bump is not completely eliminated by pulsed-light treatment, it at least does not grow.

Task Deliverable

The statement of work for the pulsed-light annealing task calls out a final deliverable for the pulsed-light annealing task consisting of "fabrication of a CIGS device on a polyimide foil substrate where the CIGS was formed using pulsed-light Rapid Thermal Annealing." Table 1 summarizes the precursor-film conversion experiments performed as part of the second round of pulsed-light annealing experiments. For device fabrication, we need a CIGS film that is single-phase with a chalcopyrite structure and is not unduly suffering from delamination or blistering. The films that come closest to meeting these criteria are the ones made from type E precursor structures. We are therefore in the process of finishing into devices three of the type E samples on polyimide as well as one type E sample on stainless steel. As XRD indicates that these films contain a very small but detectable amount of copper selenide, it is likely that all the devices produced from these films may be dead. If any devices are alive, the best will be submitted as a final task deliverable with a separate letter describing its performance.

Table 1: Summary of results for precursor film conversion in the second round of pulsed-light annealing experiments. Phases in parentheses were observable only as a minor bump or shoulder on another peak in the XRD spectra.

Sample #	Film type	Substr.	Modeled T (C)	Appearance	Phases detected by XRD
46NE	C	SS	563	blistering on one edge	CIGS, Se, Cu_3Se_2
47NW	C	SS	646	blistering on edges	Cu_3Se_2, CIGS
47SW	C	PI	557	slight blistering on edges	Cu_3Se_2, CIGS, $MoSe_2$, In_2Se_3
46SE	C	PI	612	some delamination	Cu_3Se_2, CIGS, $MoSe_2$
49NE	D	SS	559	very blistered	CIGS, Cu_3Se_2
49NW	D	SS	648	very blistered	CIGS, (Cu_3Se_2)
51NW	D	SS	800	speckled and colored	
51SE	D	PI	560	blistered	Se, CIGS, Cu_3Se_2, In_2Se_3
49SE	D	PI	613	very blistered	
51SW	D	PI	520	slight blistering	CIGS, Se, Cu_3Se_2
54NW	E	SS	564	delamination on corner	CIGS, (Cu_3Se_2)
55NE	E	SS	702	brown with delaminated spots	CIGS
54SE	E	PI	522	shiny like as-deposited film	CIGS, (Cu_3Se_2)
54SW	E	PI	563	lots of delamination	CIGS, (Cu_3Se_2)
55SW	E	PI	620	slight blistering on edges	CIGS, (Cu_3Se_2)

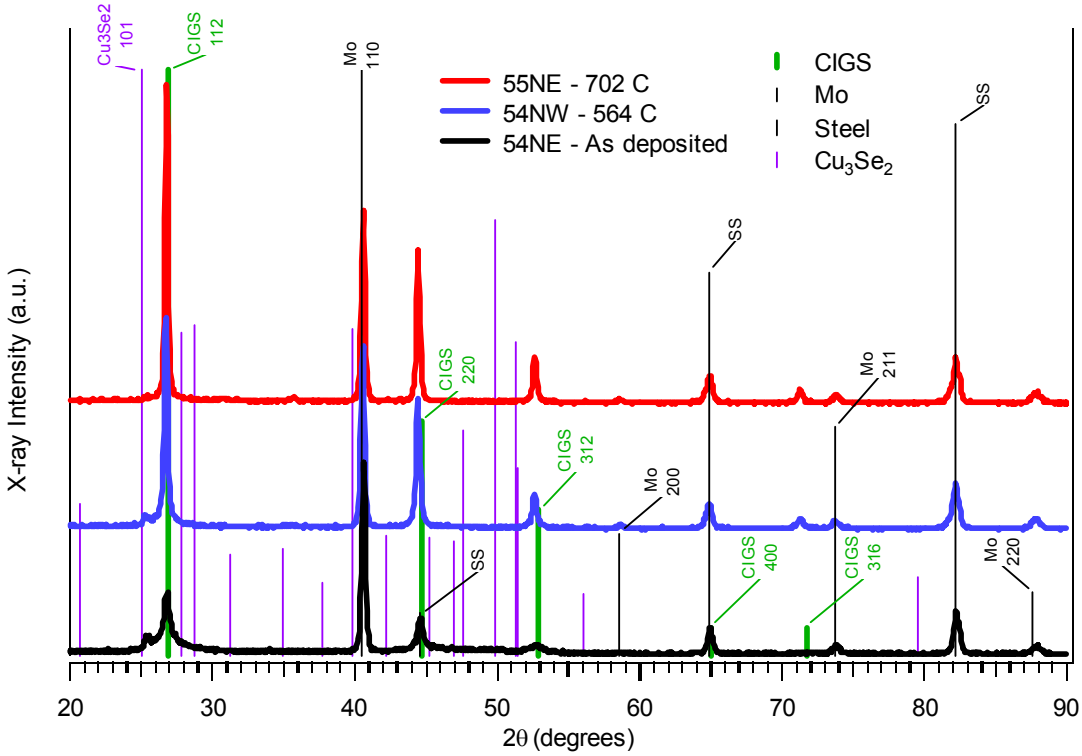

Figure 5: XRD spectra of <u>type E</u> precursor films on <u>stainless steel</u> substrates in the as-deposited state and after pulsed-light annealing.

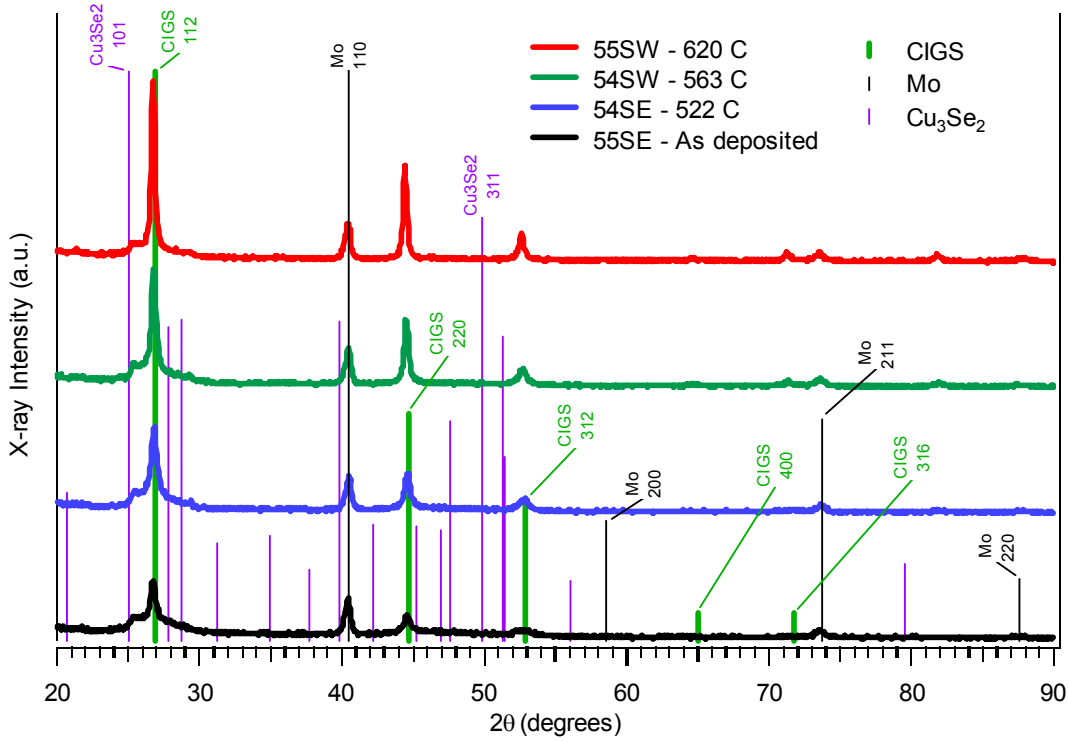

Figure 6: XRD spectra of <u>type E</u> precursor films on <u>polyimide</u> substrates in the as-deposited state and after pulsed-light annealing.

Pulsed-light annealing of evaporated CIGS films

ITN is interested in the potential of pulsed-light annealing in CIGS processing not only for the formation of CIGS from precursor films, but also for treatment of fully-formed single-phase CIGS films such as those produced in the standard co-evaporation process. Pulsed-light annealing may potentially be used to heat CIGS films to higher temperatures than they could be subjected to during their deposition. With co-evaporation of CIGS films on polyimide, for instance, the substrate temperature is normally limited to 450 °C, as higher temperatures will damage the polyimide. Very briefly heating a CIGS film on polyimide to 550 or 600 °C with pulsed-light annealing, however, potentially could be tolerated by the substrate and could potentially anneal away some of the defects in the CIGS that come with deposition at a lower-than-ideal temperature.

Large sheets of co-evaporated CIGS films produced in production equipment at Global Solar Energy (GSE) on polyimide and on stainless steel substrates were obtained for this investigation. Film quality before pulsed-light annealing was tested by fabricating devices on samples cut from these sheets adjacent to the areas to be used for the pulsed-light annealing experiments. Most devices on the SS substrate were found to have efficiencies in the range of 10.5% to 12.5%. Devices on the PI substrate predominantly had efficiencies in the range of 6% to 8%. Following this initial quality test, four samples of CIGS on PI and four samples of CIGS on SS were cut out for the pulsed-light annealing investigation. All eight samples were then sent by mail to the laboratory where pulsed-light annealing was to be performed. Two of the samples on SS and two of the samples on PI were each subjected to a single light pulse with a 20-ms duration. Pulse fluence values were selected so as to produce maximum film temperatures of 500 °C and 560 °C for the samples with PI substrates and 705 °C and 809 °C for the samples with SS substrates. The other four samples were not subjected to pulsed-light annealing and instead served as “traveling control” pieces. All samples were then shipped back to ITN where they were finished into devices.

Figure 7 and Figure 8 shows the performance parameters under simulated AM1.5 illumination for the devices made on the CIGS-on-SS samples and the CIGS-on-PI samples, respectively. It must be noted that the devices on the control samples have efficiencies that are substantially less than the efficiencies obtained when quality-checking the material, especially for the CIGS-on-SS samples. This suggests that shipment and handling of the samples had a strong effect on the device performance or that something went wrong in device finishing. Devices on the CIGS-on-SS sample heated to 705 °C (as indicated by thermal modeling) have efficiencies less than 1%, and devices on the sample heated to 809 °C are essentially dead. We did not have the time or resources remaining on the program to investigate the causes of these poor cell results, but possibilities include loss of selenium and/or excessive oxidation at the film surface. For the CIGS-on-PI samples, heating of the films to 500 °C or 560 °C with pulsed-light annealing appears to have slightly reduced device performance primarily through the lowering of fill factor. An important positive result, however, is that treatment even at 560 °C did not make the substrate brittle or significantly deformed, which demonstrates the viability of using pulsed-light annealing to heat CIGS films on polyimide to higher temperature than could normally be used during deposition.

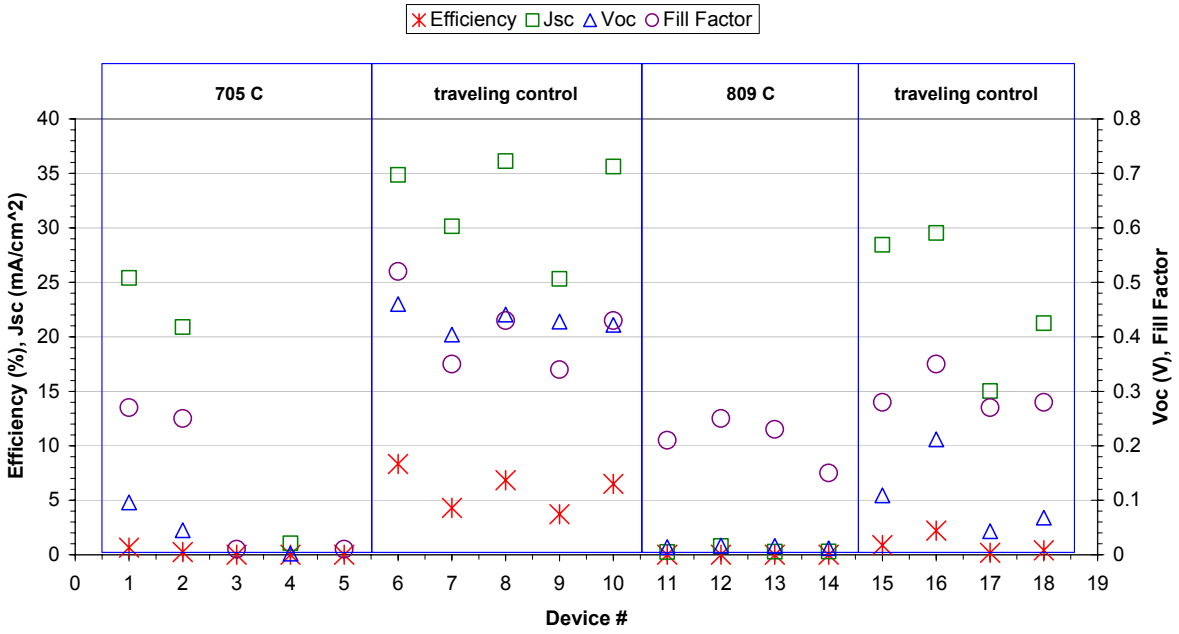

Figure 7: Device performance parameters for devices made from evaporated-CIGS films on <u>stainless steel</u> substrates. Blue boxes group devices on a single sample. Two samples were subjected to pulsed-light annealing with one heated to 705 °C and the other to 809 °C. The other two samples did not receive pulsed-light annealing.

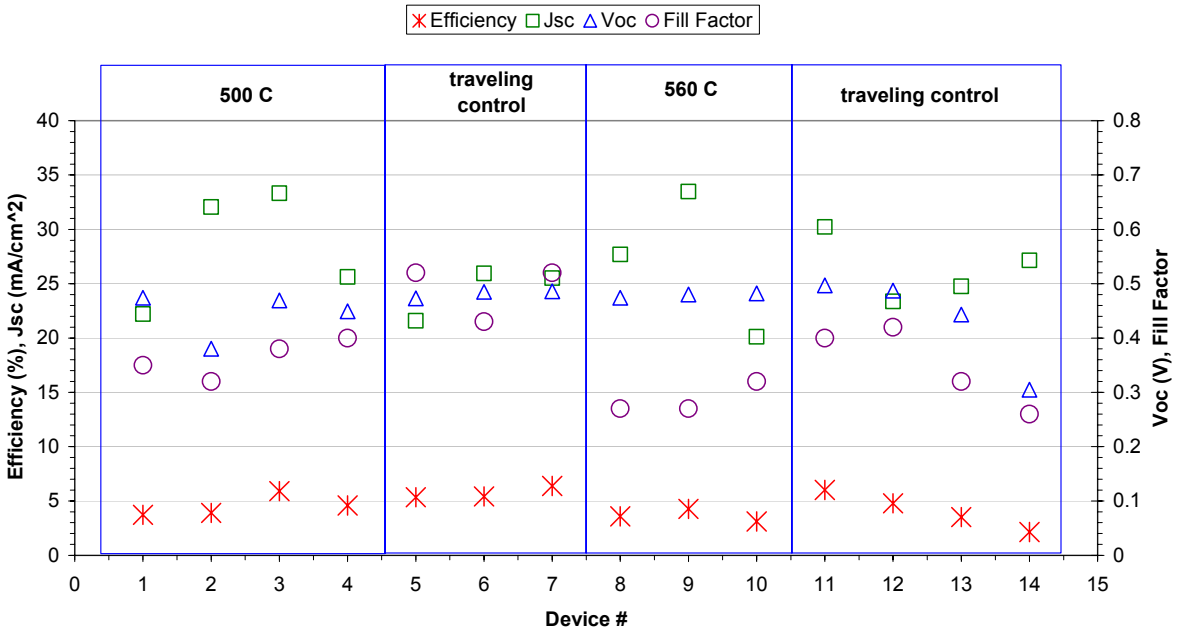

Figure 8: Device performance parameters for devices made from evaporated-CIGS films on <u>polyimide</u> substrates. Blue boxes group devices on a single sample. Two samples were subjected to pulsed-light annealing with one heated to 500 °C and the other to 560 °C. The other two samples did not receive pulsed-light annealing.

Summary

This report marks the end of the pulsed-light annealing task of ITN's PACE project, which is funded under NREL's Thin Film Photovoltaic Partnership Program. With this task, we have demonstrated that pulsed-light annealing can be used to convert CIGS precursor films to single-phase or nearly single-phase CIGS films in the chalcopyrite structure desired for solar cell fabrication. Conversion to CIGS can take place with heating times on the order of tens of milliseconds given that the precursor film has an appropriate structure. An attempt to produce solar cells from CIGS films formed in this manner is underway and, if successful, will result in production of the final deliverable for this task. Subjecting CIGS films produced by co-evaporation to pulsed-light annealing generally resulted in lower device performance. Nonetheless, it was demonstrated that pulsed-light annealing of CIGS films on polyimide could be used to heat the films to higher temperatures than could normally be used during deposition without substrate damage. Given that higher substrate temperature during deposition generally results in higher efficiency devices, it seem plausible that with sufficient control of the ambient environment, pulsed-light annealing might someday be used to improve CIGS quality after deposition.

Best Wishes,

Garth Jensen
Co-Principal Investigator
ITN Energy Systems

Cc: Ms. Carolyn Lopez; NREL contracts and business services